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Study of the Effective Pair Interatomic Interaction in a Co–Ni Melt in Terms of the Wills–Harrison Model

N. E. Dubinin

Ural Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia

e-mail: ned67@mail.ru

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Abstract—The dependence of the effective partial Wills–Harrison pair potentials in the equiatomic Co–Ni melt near the melting temperature on the probability of the existence of both diagonal and nondiagonal (in magnetic quantum number) overlappings of *d* electrons located at different atoms in the molten metal is analyzed.

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INTRODUCTION

The model proposed by Wills and Harrison (WH) [1] to calculate the internal energy and the effective pair interatomic interaction in transition metals is widely used to study transition-metal melts [2–8].

In [9], we suggested a corrected WH model: the effective *d–d* electron–electron interaction in a metal takes into account the contributions caused by the nondiagonality in a magnetic quantum number.

Since the degree of this nondiagonality is unknown, we introduced the probability p of the existence of nondiagonal *d–d* electron overlappings between two atoms in a metal provided they are equally probable between each other and with diagonal overlappings. Then, the WH model that takes into account only five equally probable diagonal *d–d* overlappings is valid at $p = 0$, and the fully corrected WH model with 25 equally probable (5 diagonal and 20 nondiagonal) overlappings holds true at $p = 1$.

In this work, we apply this correction to calculate partial Wills–Harrison pair potentials for the equiatomic Co–Ni melt and analyze how a change in p influences their characteristics.

THEORY

The partial WH pair potential for a binary system $\varphi_{ij\mathrm{WH}}(r)$ is written as [7]

$$\varphi_{ij\mathrm{WH}}(r) = \varphi_{sij}(r) + \varphi_{dij}(r), \qquad (1)$$

where $\varphi_{sij}(r)$ and $\varphi_{dij}(r)$ $(i, j = 1, 2)$ are the contributions induced by the *s* and *d* electron states, respectively.

Contribution $\varphi_{sij}(r)$ is calculated in terms of the second order of the perturbation theory in pseudopotential (hereafter, in atomic units (a.u.)),

$$\varphi_{sij}(r) = \frac{z_{si}z_{sj}}{r} + \frac{1}{8\pi^2\rho}\int_0^\infty F_{ij}(q)\frac{\sin(qr)}{qr}q^2\mathrm{d}q, \qquad (2)$$

where ρ is the mean atomic density, z_{si} is the effective *s* electron valence of a pure metal of the *i*th kind, and $F_{ij}(q)$ is the partial characteristic function

$$F_{ij}(q) = -\frac{q^2\omega_i(q)\omega_j(q)}{\pi\rho[(\varepsilon(q)-1)^{-1}+1-f(q)]}. \qquad (3)$$

Here, $\varepsilon(q)$ is the Hartree dielectric function, $f(q)$ is the exchange-correlation function taken in the Vashishta–Singwi approximation [10], and $\omega_i(q)$ is the form factor of the pseudopotential of an unscreened ion of the *i*th kind in the binary system.

Following [6], we use the local Brettonet–Silbert (BS) model pseudopotential [11] generalized to binary systems in [12],

$$\omega_{i\mathrm{BS}}(r) = \begin{cases} \sum_{n=1}^{2} B_{ni}\exp\left(\dfrac{r}{na_i}\right), & r \le R_{\mathrm{C}i} \\ -z_{si}/r, & r \ge R_{\mathrm{C}i} \end{cases}, \qquad (4)$$

where R_{Ci} and a_i are the BS model pseudopotential parameters and B_{1i} and B_{2i} are the coefficients found from the condition of continuity of $\omega_{i\mathrm{BS}}(r)$ and its first derivative at $r = R_{Ci}$,

$$\begin{aligned} B_{1i} &= (z_{si}/R_{\mathrm{C}i})(1-2a_i/R_{\mathrm{C}i})\exp(R_{\mathrm{C}i}/a_i), \\ B_{2i} &= (2z_{si}/R_{\mathrm{C}i})(a_i/R_{\mathrm{C}i}-1)\exp(0.5R_{\mathrm{C}i}/a_i). \end{aligned} \qquad (5)$$

Input data used for the calculation

Metal	z_{si}	z_{di}	r_{di} (a.u.)	R_{Ci} (a.u.)	a_i (a.u.)	ρ (a.u.)
Co	1.4	7.6	1.437	1.641	0.393	0.011648
Ni	1.4	8.6	1.342	1.030	0.207	0.011732

Form factor $\omega_{i\mathrm{BS}}(q)$ is determined from the expression

$$\omega_{i\mathrm{BS}}(q) = 4\pi\rho a_i^3\left[\frac{B_{1i}J_{1i}(q)}{(1+a_i^2q^2)^2} + \frac{8B_{2i}J_{2i}(q)}{(1+4a_i^2q^2)^2}\right] - (4\pi\rho z_{si}/q^2)\cos(qR_{Ci}), \quad (6)$$

where

$$J_{1i}(q) = 2 - \exp\left(-\frac{R_{Ci}}{a_i}\right)\left\{\left[R_{Ci}\frac{1+a_i^2q^2}{a_i} + 1 - a_i^2q^2\right] \times \frac{\sin(qR_{Ci})}{a_iq} + \left[2 + \frac{R_{Ci}(1+a_i^2q^2)}{a_i}\right]\cos(qR_{Ci})\right\};$$

$$J_{2i}(q) = 2 - \exp\left(-\frac{R_{Ci}}{2a_i}\right)\left\{\left[R_{Ci}\frac{1+4a_i^2q^2}{2a_i} + 1 - 4a_i^2q^2\right] \times \frac{\sin(qR_{Ci})}{2a_iq} + \left[2 + \frac{R_{Ci}(1+4a_i^2q^2)}{2a_i}\right]\cos(qR_{Ci})\right\}.$$

Partial pair potential $\varphi_{dij}(r)$ entering in the right-hand side of Eq. (1) consists of the following two parts:

$$\varphi_{dij}(r) = \varphi_{bij}(r) + \varphi_{cij}(r), \quad (7)$$

where $\varphi_{bij}(r)$ is the contribution caused by the presence of a *d* band with a finite width in the metal and $\varphi_{cij}(r)$ is the contribution induced by the displacement of the center of the *d* band due to the nonorthogonality of the *d* states in the metal. We have

$$\varphi_{bij}(r) = -\bar{z}_d\left(\frac{10-\bar{z}_d}{10}\right)\left(\frac{12}{\nu_{ij}}\right)^{1/2}\frac{(r_{di}r_{dj})^{3/2}}{r^5}K_b, \quad (8)$$

$$\varphi_{cij}(r) = \bar{z}_d\frac{(r_{di}r_{dj})^3}{r^8}K_c. \quad (9)$$

Here, $\bar{z}_d = c_1z_{d1} + c_2z_{d2}$ (z_{di} is the effective *d* electron valence of the pure metal of the *i*th kind, c_i is the concentration of the component of the *i*th kind in the binary system), r_{di} is the parameter having the physical meaning of the radius of the *d* state of the free atom of the *i*th kind, ν_{ij} is the partial coordination number, and K_b and K_c are the coefficients written in the form proposed in [9]. They are

$$K_b = \left[\frac{1}{5}\left(\left(1-\frac{4p}{5}\right)y_0^2 + \left(2-\frac{6p}{5}\right)(y_2^2+y_1^2) + \frac{4p}{5}y_0(y_1+y_2) + \frac{8p}{5}y_1y_2\right)\right]^{\frac{1}{2}}, \quad (10)$$

$$K_c = -\frac{2}{5}\left[\left(1-\frac{4p}{5}\right)y_0x_0 + \left(2-\frac{6p}{5}\right)(y_1x_1+y_2x_2) + \frac{2p}{5}(y_0(x_1+x_2)+x_0(y_1+y_2)) + \frac{4p}{5}(y_1x_2+y_2x_1)\right], \quad (11)$$

where $y_m = y_{|m|}$ and $x_m = x_{|m|}$ are the coefficients depending on quantum number *m*,

$$y_m = -\frac{(-1)^m180}{\pi(2+m)!(2-m)!}, \quad (12)$$

$$x_m = -\frac{1}{8}\left(1+\frac{4m^2-1}{9}\right)y_m. \quad (13)$$

RESULTS AND DISCUSSION

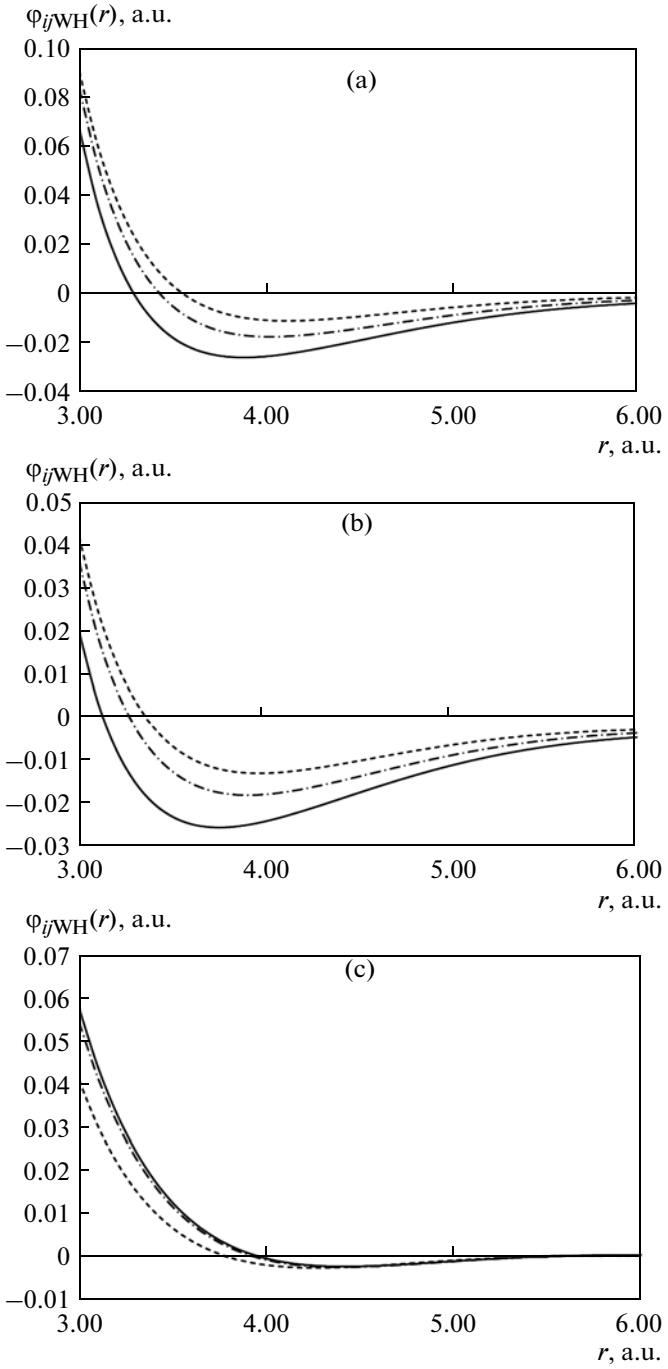
The WH partial pair potentials in the equiatomic Co–Ni melt were calculated near the melting temperature at various values of *p*.

The table gives r_{di} and z_{si} taken from [1] and [13], respectively, and $z_{di} = z_i - z_{si}$ (where z_i is the total valence of the pure metal of the *i*th kind) and the BS model pseudopotential parameters borrowed from [13], where they were determined for pure liquid metals. The mean atomic density of a binary melt is taken to be additive with respect to the corresponding values of ρ of the pure metals (which were experimentally obtained in [14] at $T = 1823$ K for Co and at $T = 1773$ K for Ni), which is allowable due to the closeness of these values (see table). The values of all three ν_{ij} are assumed to be 12.

The obtained pair potentials are shown in the figure. As in the case of pure metals [9], an increase in *p* for all potentials decreases the depth of the first minimum of the pair potential, weakly affects its coordinate when *p* changes from 0 to 0.5, and significantly shifts its position toward large *r* at $p = 1$ as compared to the case at $p = 0.5$.

It was also found that the ordering potential $V = \varphi_{12}(r) - (\varphi_{11}(r) + \varphi_{22}(r))/2$ at $p = 0$ and $p = 0.5$ is close to zero ($V \approx 0$), which indicates almost ideal mixing of the components, whereas a tendency toward separation ($V > 0$) takes place at $p = 1$.

The tendency toward separation in the liquid phase is unlikely in the Co–Ni system, since it follows from the Co–Ni phase diagram [15] that Co and Ni are infinitely dissolved in each other in the crystalline state and form a continuous series of solid solutions. Thus, the result obtained can indicate that the nondiagonal *d*–*d* overlappings between different atoms do not gen-



Partial WH pair potentials in the equiatomic Co–Ni melt near the melting temperature: (solid line) $\varphi_{Co-Co}(r)$, (dot-and-dash line) $\varphi_{Co-Ni}(r)$, and (dashed line) $\varphi_{Ni-Ni}(r)$ at p = (a) 0, (b) 0.5, and (c) 1.

erate a predominant contribution to the effective *d–d* electron interaction in the liquid metal.

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REFERENCES

1. J. M. Wills and W. A. Harrison, "Interionic interactions in transition metals," Phys. Rev. B **28**, 4363–4373 (1983).
2. C. Hausleitner and J. Hafner, "Soft-sphere reference system in thermodynamic variational calculations. II: Liquid transition metals," J. Phys. F: Metal Phys. **18**, 1025–1035 (1988).

3. C. Regnaut, "Analysis of the liquid structure of 3*d* transition metals from the Wills–Harrison model," Z. Phys. B **76**, 179–184 (1989).
4. J. L. Bretonnet and A. Derouiche, "Variational thermodynamic calculations for liquid transition metals," Phys. Rev. B **43**, 8924–8929 (1991).
5. C. Hausleitner, G. Kahl, and J. Hafner, "Liquid structure of transition metals: investigations using molecular dynamics and perturbation- and integral-equation techniques," J. Phys. F: Condens. Matter **3**, 1589–1602 (1991).
6. N. E. Dubinin, L. D. Son, and N. A. Vatolin, "The Wills–Harrison approach to the thermodynamics of binary liquid transition-metal alloys," J. Phys. F: Condens. Matter **20**, 114111 (2008).
7. N. E. Dubinin, "Thermodynamics of liquid Fe–Ni alloys: calculations at different temperatures," J. Phys.: Conf. Series, **144**, 012115 (2009).
8. N. E. Dubinin, "Interatomic pair interaction in liquid transition metals," Acta Physica Polonica **115** (4), 783–785 (2009).
9. N. E. Dubinin, "Account of non-diagonal coupling between *d* electrons at describing the transition-metal pair potentials," J. Phys.: Conf. Series **338**, 012004 (2012).
10. P. Vashishta and K. Singwi, "Electron correlation at metallic densities," Phys. Rev. B **6**, 875–887 (1972).
11. J. L. Bretonnet and M. Silbert, "Interionic interactions in transition metals. Application to vanadium," Phys. Chem. Liq. **24**, 169–176 (1992).
12. N. E. Dubinin, L. D. Son, and N. A. Vatolin, "Thermodynamic properties of liquid binary transition-metal alloys in the Bretonnet–Silbert model," Defect and Diffusion Forum **263**, 105–110 (2007).
13. N. Jakse and J. L. Bretonnet, "Structure and thermodynamics of liquid transition metals: integral-equation study of Fe, Co and Ni," J. Phys.: Condens. Matter **7**, 3803–3815 (1995).
14. Y. Waseda, *The Structure of non-Crystalline Materials—Liquids and Amorphous Solids* (McGraw-Hill, New York, 1981).
15. *Phase Diagrams of Binary Metallic Systems: a Handbook*, Ed. by N. P. Lyakishev (Mashinostroenie, Moscow, 1997), Vol. 2.

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